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THE MILLIMETER- AND SUBMILLIMETER-WAVE SPECTRUM OF ETHYLENE OXIDE (c-C_2H_4O)

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ABSTRACT

The cyclic molecule ethylene oxide (c-C_2H_4O) has recently been detected in the interstellar source Sgr B2N. Previous laboratory work on the rotational spectrum of this molecule extends only to a frequency of 123 GHz. We report here the extension of the laboratory rotational spectrum of this species through the frequency range 262–358 GHz using a new fast scan spectrometer (FASSST). The newly measured lines have been combined with previous data at lower frequencies to form a data set consisting of 662 lines that has been assigned and fitted via a standard semirigid asymmetric top analysis. The spectral constants obtained from the fit have allowed us to predict the frequencies of many additional lines.

Subject headings: ISM: molecules — methods: laboratory — molecular data — radio lines: ISM

1. INTRODUCTION

Ethylene oxide (c-C_2H_4O), a small cyclic molecule, is a "metastable" isomer of acetaldehyde (CH_3CHO), lying more than 1 eV higher in energy than the lowest energy form. Interestingly, ethylene oxide is kinetically stable in the laboratory, whereas a lower energy metastable isomer—vinyl alcohol (CH_2CHOH)—requires unusual conditions for its laboratory preparation because it tends to isomerize into acetaldehyde. Acetaldehyde has been detected in the interstellar medium, while earlier searches for ethylene oxide and vinyl alcohol had not been successful (Irvine et al. 1989; Hollis et al. 1980). Recently, however, Dickens et al. (1997) detected 10 rotational transitions of ethylene oxide in the source Sgr B2N and deduced a rotational temperature of 18 K and a column density of 3.3×10^{14} cm^{-2}.

Despite the rather low rotational temperature, which is consistent with other oxygen-containing molecules found in Sgr B2N, this source is considered to be of the "hot core" type (Miao et al. 1995) and is known to be the home for a variety of complex hydrogenated species. Although the chemistry of such regions is far from understood (Charnley et al. 1995; Caselli, Hasegawa, & Herbst 1993; Brown, Charnley, & Millar 1988), the general picture is one in which rising temperatures associated with star formation drive previously synthesized molecules off the grains into the gas, where they are the precursors for a high-temperature gas-phase chemistry. The precursor molecules can be synthesized directly on grains or in the gas followed by adsorption onto the cold dust particles. Strong laboratory evidence for formation on cold grains has been found for the molecule methanol, which can be directly synthesized via successive H atom additions to condensed CO (Hiraoka et al. 1994; Charnley, Tielens, & Rogers 1997) as long as the temperature is low enough for CO to remain on dust surfaces (Caselli et al. 1993). Once methanol is released into the gas, it acts as a precursor for a variety of oxygen-containing organic molecules (Millar, Herbst, & Charnley 1991; Blake et al. 1987). Whether or not such a scenario pertains to ethylene oxide is uncertain, since the specific gas phase reactions for its formation are not well studied.

The rotational spectrum of ethylene oxide in its ground vibrational state has been studied through 123 GHz by a number of investigators, most recently by Creswell & Schwendeman (1974) and by Hirose (1974). References to earlier work can be found in Townes & Schawlow (1975). The molecule is a semirigid asymmetric top which is oblate in character, and the analysis of its rotational spectrum can be handled by standard means. The transitions are all b-type in character; the dipole moment, μ_b, is 1.89 D (Cunningham et al. 1951). Using the constants reported by Hirose (1974), Dickens et al. (1997) calculated frequencies for transitions through 300 GHz, with estimated uncertainties less than 1 MHz for transitions up to $J = 10$, an estimate confirmed by a preliminary version of the analysis discussed here. In this paper, we report the measurement and assignment of over 500 rotational transitions in the frequency range 262–358 GHz for $J < 50$. These lines have been added to many of the previously measured lower frequency lines to form a global data set of 662 transitions, which has been fitted to experimental accuracy. The spectral constants determined from the fit have allowed us to predict accurately a large number of lines through 400 GHz in frequency.

2. EXPERIMENT AND SPECTRAL ANALYSIS

The spectrum of ethylene oxide in the frequency range 262–358 GHz has been taken with a new type of fast scan submillimeter system that we have dubbed FASSST (fast scan submillimeter spectroscopic technique; Petkie et al. 1997). In this system, the submillimeter-wave radiation is provided by a voltage-tunable backward wave oscillator (BWO), which is scanned rapidly through a large frequency range. The frequencies are calibrated optically by use of a Fabry-Perot cavity. Since the sweep is so rapid, frequency

TABLE 1

ASSIGNED AND FITTED TRANSITION FREQUENCIES OF ETHYLENE OXIDE IN THE GROUND VIBRATIONAL STATE

J'	K'_a	K'_c	J''	K''_a	K''_c	Measured Frequency (MHz)	Calculated Frequency (MHz)	$O-C$ (MHz)	Reference[a]
3	3	0	3	2	1	23134.160	23134.215	−0.055	1, 2
3	2	1	3	1	2	23610.420	23610.370	0.050	1, 2
4	3	1	4	2	2	24834.300	24834.257	0.043	1, 2
2	1	1	2	0	2	24923.690	24923.644	0.046	1, 2
6	0	6	5	3	3	26267.940	26267.982	−0.042	2
5	4	1	5	3	2	29687.080	29687.034	0.046	1, 2
4	0	4	3	3	1	33588.910	33588.972	−0.062	2
4	4	0	4	3	1	34147.760	34147.727	0.033	1, 2
2	2	1	2	1	2	34157.040	34156.986	0.054	1, 2
6	4	2	6	3	3	35790.570	35790.548	0.022	1, 2
7	5	2	7	4	3	37328.780	37328.826	−0.046	1, 2
5	3	2	5	2	3	37780.740	37780.693	0.047	1, 2
6	5	1	6	4	2	38701.050	38701.078	−0.028	1, 2
1	1	1	0	0	0	39581.640	39581.607	0.033	1, 2
3	3	1	3	2	2	39680.050	39680.087	−0.037	1, 2
4	2	2	4	1	3	41579.440	41579.454	−0.014	1
3	1	2	3	0	3	45177.530	45177.565	−0.035	1
4	4	1	4	3	2	47094.930	47094.971	−0.041	1
5	5	0	5	4	1	47556.890	47556.920	−0.030	1
3	2	2	3	1	3	49000.880	49000.971	−0.091	1

NOTE.—Table 1 appears in its entirety in the electronic edition of the Astrophysical Journal.

[a] The lack of a reference indicates that the line is reported here for the first time.

REFERENCES.—(1) Hirose 1974; (2) Creswell & Schwendeman 1974.

drifts and instabilities are frozen out, and there is no need for active frequency stabilization. With the new system, it is possible to measure thousands of spectral lines each second, with a typical accuracy of ≈ 0.1 MHz. In the spectral region studied, we were able to assign all of the strong lines and approximately 50% of the total of all lines detected; the remaining weak lines are mainly from excited vibrational states.

TABLE 2

SPECTROSCOPIC PARAMETERS FOR ETHYLENE OXIDE IN THE GROUND VIBRATIONAL STATE

Parameter	Value[a]
A (MHz)	25483.88812(224)
B (MHz)	22120.84830(224)
C (MHz)	14097.83999(271)
Δ_J (kHz)	51.1883(173)
Δ_{JK} (kHz)	−70.4938(116)
Δ_K (kHz)	27.6541(226)
δ_J (kHz)	−9.01689(109)
δ_K (kHz)	3.3491(118)
Φ_J (Hz)	0.2456(483)
Φ_{JK} (Hz)	−5.2164(452)
Φ_{KJ} (Hz)	15.7370(964)
Φ_K (Hz)	−10.638(121)
ϕ_J (Hz)	−0.05097(206)
ϕ_{JK} (Hz)	1.4297(327)
ϕ_K (Hz)	−17.8633(989)
L_J (mHz)	−0.1210(427)
L_{JJK} (mHz)	−0.1288(397)
L_{JK} (mHz)	0.624(179)
L_{KKJ} (mHz)	−0.800(293)
L_K (mHz)	0.892(251)
l_J (mHz)	−0.00367(120)
l_{JK} (mHz)	0.0921(250)
l_{KJ} (mHz)	−0.448(121)
l_K (mHz)	0.679(193)
P_K (μHz)	−1.114(172)
σ[b]	1.38

[a] Standard error in units of last digit in parentheses; III*l* basis used.

[b] Weighted standard deviation (dimensionless).

The measured and assigned lines, along with previous data at lower frequencies, were combined into a global data set of 662 transitions and fit to an asymmetric top Hamiltonian with centrifugal distortion using Watson's A reduction (Watson 1977). A root mean square deviation of 138 kHz was determined by the fit, which is comparable with the experimental uncertainty in the lines. The fitted spectral transitions are listed in Table 1 (only the first 20 rows of Table 1 appear in the paper edition; for the complete version, see the electronic edition) along with quantum assignments, residuals (observed minus calculated frequencies), and, for previously measured lines, the most recent reference. The spectroscopic constants determined by the fit are listed in Table 2. These include the standard rotational constants, full sets of fourth-order, sixth-order, and eighth-order centrifugal distortion constants, and one tenth-order constant.

3. DISCUSSION

Using the spectroscopic constants in Table 2, we can predict the frequencies of unmeasured lines both outside of the measured frequency range and/or, to a limited extent, involving higher quantum numbers than the measured transitions. These are listed in Table 3 (only the first 20 rows of Table 3 appear in the paper edition; for the complete version, see the electronic edition), which contains quantum assignments, predicted frequencies and uncertainties, intensities, and upper state energies. The intensities are expressed as S-values (Townes & Schawlow 1975) multiplied by the square of the dipole moment in units of debye squared. Only transitions with rotational quantum number $J \leq 60$, $\mu^2 S \geq 0.10$, $E_{\rm upper} \leq 700$ cm^{-1}, frequency ≤ 400 GHz, and predicted uncertainty less than 0.5 MHz are included in Table 3 (a more complete table is also available from the

TABLE 3

PREDICTED TRANSITION FREQUENCIES OF ETHYLENE OXIDE IN THE GROUND VIBRATIONAL STATE

J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency (MHz)	Uncertainty (MHz)	$\mu^2 S$	$E_{\rm upper}$ ($\rm cm^{-1}$)
1	1	0	1	0	1	11385.905	0.001	5.36	1.588
2	2	0	2	1	1	15603.557	0.002	7.33	4.792
3	3	0	3	2	1	23134.215	0.003	7.59	9.660
3	2	1	3	1	2	23610.370	0.004	9.23	8.888
4	3	1	4	2	2	24834.257	0.003	13.08	15.087
2	1	1	2	0	2	24923.644	0.004	4.59	4.272
5	4	1	5	3	2	29687.034	0.003	14.83	22.918
4	4	0	4	3	1	34147.727	0.005	7.03	16.227
2	2	1	2	1	2	34156.986	0.004	2.98	4.608
6	4	2	6	3	3	35790.548	0.005	17.66	31.139
7	5	2	7	4	3	37328.826	0.004	21.26	41.942
5	3	2	5	2	3	37780.693	0.006	12.63	21.927
6	5	1	6	4	2	38701.078	0.006	14.56	32.430
1	1	1	0	0	0	39581.607	0.005	3.57	1.320
3	3	1	3	2	2	39680.086	0.004	4.61	9.556
4	2	2	4	1	3	41579.454	0.007	7.90	14.259
8	6	2	8	5	3	43397.469	0.005	22.31	54.395
3	1	2	3	0	3	45177.565	0.007	3.96	8.100
4	4	1	4	3	2	47094.971	0.005	5.53	16.177
9	6	3	9	5	4	47145.517	0.005	26.27	66.745

NOTE.—Table 3 appears in its entirety in the electronic edition of the Astrophysical Journal.

authors). Those assigned and fitted lines listed in Table 1 that meet the constraints are included in Table 3 with their predicted frequencies so that the additional information concerning these lines (intensities, upper state energies) is readily available for astronomical use. A comparison of those frequencies in Table 3 corresponding with the predictions in Tables 1 and 2 of Dickens et al. (1997) shows that the predicted frequencies of these authors, based on the earlier data of Hirose (1974), are generally accurate to 1 MHz for low J-values.

In computing the actual line intensities, the nuclear spin statistics of the hydrogen nuclei must be considered. The different rotational quantum states possess different spin weights due to the C_{2v} symmetry of the molecule and the existence of four hydrogen nuclei, each with spin $I = \frac{1}{2}$. These spin weights are 10 for states in which the K_a and K_c quantum numbers are both odd or both even, and 6 for states in which one of these quantum numbers is odd and the other even. Note that b-type transitions occur between states with the same spin weights.

The partition function, q, for the rotational levels of the ground vibrational state of ethylene oxide is well approximated by the standard asymmetric top expression (Townes & Schawlow 1975) multiplied by the total spin weight, $(2I + 1)^4 = 16$, and divided by the symmetry number, $\sigma = 2$. The result is $q = 15.13T^{3/2}$, where T is the temperature in kelvins. The fractional population f for any rotational state is then given by the expression

$$f = g_s(2J + 1) \exp(-E/kT)/q , \quad (1)$$

where g_s stands for the proper spin weight (10 or 6), E is the rotational energy, and k is the Boltzmann constant.

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